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# Reactivity Assessment of Indian Biomass Ashes for Their Utilization in Alternative Cementitious Binders

**Nilakanmani Manimaran*, Manu Santhanam and Piyush Chaunsali**

*Department of Civil Engineering, IIT Madras, India*

***Correspondence to:**
Nilakanmani Manimaran
Department of Civil Engineering,
IIT Madras, India.
**E-mail:** nilakanmani@gmail.com

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## Abstract

Agro-based biomass ashes can be chemically activated with Ca-Na based activators having low alkali concentration at ambient environmental conditions to produce sustainable binders. The utilisation of agro-based biomass ash in cementitious binders is restricted due to the presence of residual carbon, inconsistency in ash composition, and variability in ash reactivity. Reactivity assessment of the biomass ash is crucial for understanding its utilization potential. This study involves physico-chemical characterization and reactivity assessment of agro-based biomass ashes collected from India. The existing reactivity assessment tools may not be suitable to assess the reactivity of pozzolanic materials for chemical activation. Hence, the reactivity is assessed by measuring the heat of hydration of chemically activated biomass ashes and lime reactivity test. The heat of hydration study is carried out without the addition of sulfates and carbonates (modified $R_3$ (Rapid, Relevant, and Reliable) method) at room temperature. The study aims at establishing composition-reactivity relationship of Indian biomass ashes.

## Keywords

Agro-based biomass ash, Chemical activation, Dissolution, Heat of hydration, Reactivity assessment

## Introduction

Global population growth, urbanization, and industrial advancements will likely increase the global energy demands up to ~20% by 2040. Biomass incineration for energy generation is increasing world-wide, particularly in developing countries like India. The global contribution of bioenergy to renewable electricity generation has increased up to 10% in 2020 - 2021 and is set to increase further [1]. Biomass constitutes 32% of primary energy consumption in India, and a major fraction (> 70 %) of the population depends on biomass for their energy demands [2, 3]. Recent studies have also identified a vast source of biomass in India and reported an annual availability of about 750 million metric tonnes [4]. This biomass is used as fuel in small-scale to medium-scale industries, agro-based industries, and energy cogeneration plants. The ash obtained from biomass combustion is pozzolanic and contains reactive silica, making it a potential candidate for cementitious binders. Utilization of high volume of agro-based biomass ash in chemically activated binders could pave a way towards sustainability of construction materials. However, the presence of unburnt carbon, variability in ash reactivity, lack of availability data, lack of processing routes to enhance reactivity, and lack of composition-reactivity-performance relationship of agro-based biomass ash hinders the overall utilisation of biomass ash in cementitious binders [5]. Due to these issues, agro-based ashes are currently disposed of in nearby landfills, posing a significant environmental concern.

Reactivity assessment of the biomass ash is crucial for understanding its utilization potential. The existing reactivity assessment tools, such as strength activity index test, Chapelle test, Frattini test, etc., may not be suitable to assess the reactivity of pozzolanic materials (like fly ash, metakaolin, rice husk ash, etc.,) for chemical activation. The strength activity index (SAI) test as per ASTM C311 [6] specifies to use Portland cement with 20% SCM (Supplementary cementitious material) as the binder to assess reactivity of the SCMs. Even the inert SCMs can sometimes pass the SAI test to attain 75% relative compressive strength. Hence, it was recommended to increase the replacement ratio of SCMs to 30% for the SAI test [7-9]. The SAI test and Frattini test quantify reactivity based on the pozzolanic reaction between calcium hydroxide from Portland cement hydration and reactive silica and reactive alumina from the SCMs. Also, these test results are a cumulative response of pozzolanic and hydraulic reactions. The longer test duration and reproducibility issues affect the practical use of the standard test methods [7-10]. Lime reactivity test as per IS 1727 produces better results which can be correlated to later age strength of blended Portland cement [8, 11]. Modified versions of lime reactivity test were also developed to help with slow reacting SCMs [10, 12, 13]. However, the variations in the binder and curing temperature for the modified test make it difficult to consider the test method for reactivity assessment. A rapid test method developed by RILEM TC 267 known as the $R_3$ test, was later standardised in ASTM C1897 – 20 [14]. $R_3$ test method recommends measuring reactivity of SCMs using heat of hydration at 40 °C [8] and bound water measurement. The binder composition consists of lime-pozzolan mix (3:1), with the addition of sulphates, carbonates, and alkali hydroxide to increase pH and replicate Portland cement system. A similar test method was also developed called the pozzolanic reactivity test/modified $R_3$ ($MR_3$) test. $MR_3$ test does not involve the addition of sulphates and carbonates to binder and the test is carried out at 50 °C, which is conducive for slow-reacting SCMs. Hence, $MR_3$ test could be better suited for alkali activated binder, as it eliminates addition of sulphates and carbonates [7, 9, 10]. This study involves physicochemical characterization and reactivity assessment of agro-based biomass ashes collected from India, to establish composition–reactivity relationship of the ashes.

# Experimentation

## Material

Agro-based biomass ashes from three different sources were collected. The fraction of ash passed through 300 µm, to remove the coarse unburnt carbon particles, was heated at 105 °C for 24 hours to remove the moisture content and was used for further testing. The biomass ashes were named as BA1, BA2, and BA3, as shown in table 1. The feedstock origin for BA1 and BA2 are mixed, which includes rice husk, sugarcane bagasse and other locally available biomass, and BA3 is sugarcane bagasse.

## Physiochemical characterization

Physical characterization of the ashes was performed to determine specific gravity and particle size distribution as shown in table 1 and figure 1. The chemical composition of the ashes was studied using X-ray fluorescence spectroscopy, mineralogical composition using X-ray diffraction, and loss on ignition (LOI) measured as per ASTM C311 [6]. The oxide composition of the ashes, reported in table 1 and figure 2, shows that most of the ashes are silicious. The sum of oxide composition requirement is fulfilled by all the ashes for Class F pozzolan ($SiO_2$ + $Al_2O_3$ + $Fe_2O_3$ > 50%) as per ASTM C 618 [15] and Silicious Fly Ash ($SiO_2$ + $Al_2O_3$ + $Fe_2O_3$ > 70%) as per IS 3812 [16]. BA3 has reported the highest alkali content (> 12 %) and $P_2O_5$ (> 3 %). The change in chemical composition is mainly due to the feedstock composition. The loss

**Table 1:** Properties of biomass ash.

| | BA1 | BA2 | BA3 |
|---|---|---|---|
| Feedstock origin | **Mixed** | **Mixed** | **Sugarcane bagasse** |
| Chemical composition by X-ray fluorescence (wt.%) | | | |
| $SiO_2$ | 79.9 | 73.1 | 66.6 |
| $Al_2O_2$ | 1.8 | 1.0 | 4.1 |
| $Fe_2O_3$ | 0.9 | 1.3 | 2.0 |
| CaO | 0.9 | 2.1 | 4.5 |
| $Na_2O$ | 0.3 | 0.2 | 0.5 |
| $K_2O$ | 3.8 | 3.8 | 11.6 |
| MgO | 1.1 | 0.9 | 3.4 |
| $P_2O_5$ | 1.8 | 1.3 | 3.1 |
| LOI% (750 °C) | 8.7 | 13.7 | 2.7 |
| Specific gravity | 2.10 | 2.07 | 2.20 |
| $D_{50}$ (µm) | 166 | 171 | 141 |

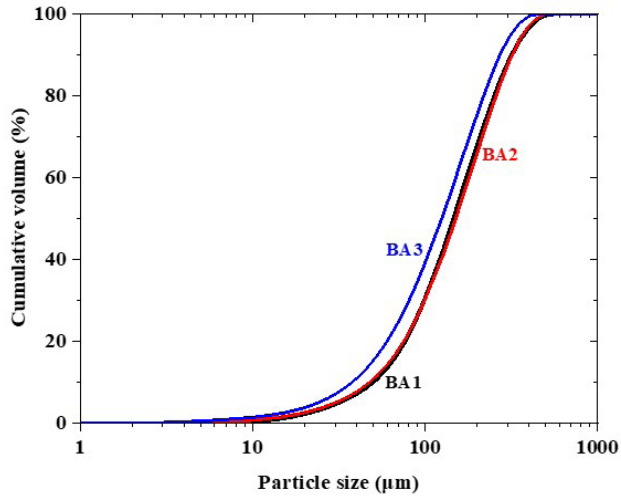


**Figure 1:** Particle size distribution of biomass ashes.

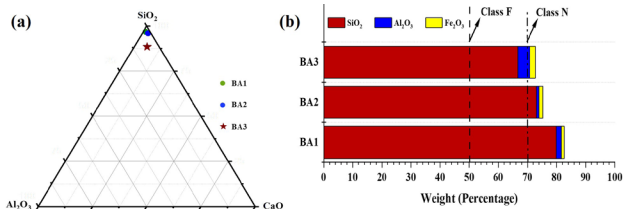


**Figure 2:** Oxide composition of the biomass ashes **(a)** ternary phase diagram of CaO-$SiO_2$-$Al_2O_3$ and **(b)** weight percentage of $SiO_2$, $Al_2O_3$, and $Fe_2O_3$.

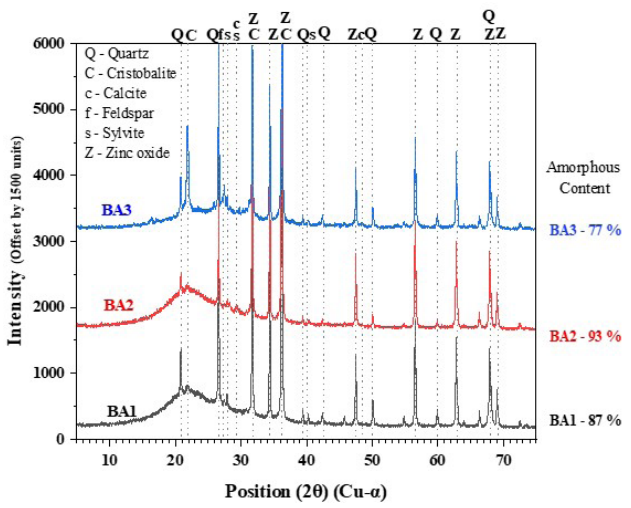


**Figure 3:** XRD patterns of biomass ashes with amorphous content.

on ignition values from table 1 show that sieving through 300 µm did not completely reduce the unburnt carbon fraction. The LOI values ranged from 3 - 14 %, with BA2 showing the highest value.

The X-ray diffraction plots showing mineralogical composition of the ashes are shown in figure 3. The amorphous hump attributing the presence of amorphous silica and unburnt carbon is observed between 20 - 30° (2θ). Zinc oxide was used as an internal standard and Rietveld refinement was used to quantify the amorphous content in the ashes. Quartz, cristobalite, feldspar, sylvite, and calcite were the crystalline phases identified. Cristobalite is formed only at high temperatures (> 800 °C) due to silica recrystallisation and cristobalite peak is only found in BA3. BA2 has the highest amorphous content.

### Reactivity assessment

Reactivity assessment of biomass ashes was performed using heat of hydration, thermogravimetric analysis, and lime reactivity test [7, 10, 11]. Heat of hydration was measured using isothermal calorimetry at 23 °C. The mix design for heat of hydration study was adapted from modified $R_3$ method (Lime: Pozzolan = 3:1; W/B = 0.9, 0.5 M and 2 M KOH solution). As per modified $R_3$ method, the test should be conducted with 0.5 M KOH solution at 50 °C. Due to certain limitations, the test was conducted at 23 °C for 7 days. After 7 dyas the binder (2 M KOH) from heat of hydration study was treated with isopropanol alcohol for hydration stoppage. Then, the binder was taken for thermogravimetric analysis to calculate portlandite consumption. The lime reactivity test was carried out as per IS 1727 [11]. Lime-pozzolan mortar cubes were cured at 25 ± 2 °C for two days before demolding and further cured at 50 °C for eight days and then tested for compressive strength.

## Results and Discussion

### Heat of hydration

The cumulative heat release measured after 7 days for BA1, BA2 and BA3 paste is shown in figure 4. The cumulative heat release is higher for 2 M paste than 0.5 M paste due to higher pH. In both molar ratios, the cumulative heat release is higher for BA2, followed by BA1 and BA3. The higher amount of amorphous content in BA1 and BA2 resulted in better reactivity of the ashes that resulted in higher cumulative heat release than in BA3. The difference in cumulative heat release values for BA2 and BA1 after 7 days decreased when the strength of the solution increased from 0.5 M to 2M. The cumulative heat release from BA3 is comparatively very less, which can be attributed to the presence of crystalline phases (cristobalite) despite the lower LOI values (< 3%). The cumulative heat release further tends to increase after 7 days, which implies that the ashes are slow reacting material at ambient temperature (23 °C). For a better degree of reaction, the test may also have to be performed at a higher temperature (e.g., 50 °C).

### Portlandite consumption

The binders prepared with 2 M KOH for heat of hydration study had better reactivity than binders with 0.5 M KOH solution. Hence, binders with 2 M KOH solution were considered for thermogravimetric analysis. The thermogravimetric analysis graphs are shown in figure 5 for the binders from heat of hydration study (2 M). The mass loss between 50 - 300 °C can be attributed to bound water and 350 - 450 °C is due to

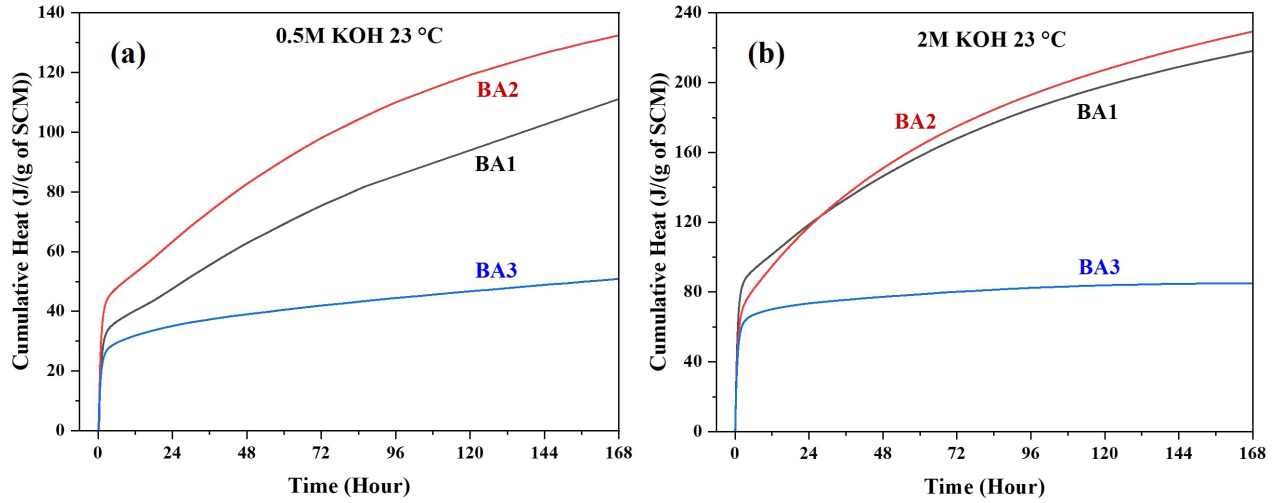


**Figure 4:** 7-day cumulative heat release for **(a)** 0.5 M paste and **(b)** 2 M paste.

**Table 2:** Portlandite consumption from TGA.

| | Portlandite consumption (g per 100 g of ash) |
|---|---|
| BA1-2M | 40 |
| BA2-2M | 41 |
| BA3-2M | 22 |

portlandite disintegration. Portlandite consumption was calculated from the initial mass of portlandite added and the final mass that remained unreacted, shown in table 2. The pozzolanic reaction between reactive silica (from ash) and portlandite to form calcium silicate hydrate, will consume the portlandite added. Higher portlandite consumption can be related to better reactivity of the ashes. Portlandite consumption for BA1 and BA2 was similar, and higher than BA3. The higher amorphous content in BA1 and BA2 lead to more consumption of portlandite, and a similar response was observed from heat of hydration experiments (cumulative heat release).

### Lime reactivity test

As per IS 1727, the mortar specimens needed to be demolded after 48 hours of casting. However, the mortar specimens could not be demolded. Therefore, BA1 and BA2 mortars were demolded after 6 days and BA3 mortar was demolded after 19 days. The presence of crystalline phases like cristobalite, comparatively less amorphous content, and phosphorus pentoxide could have been attributed for delayed setting in BA3 mortar specimens. After demolding, the specimens were cured at 90 - 100% relative humidity and 50 °C for 8 days, followed by testing. The mortar specimens took more time to set, mainly due to high water demand to obtain the required flow (70%). The porous structure of the biomass ash and high unburnt carbon content increased the water demand. The lime mortar strength test results are shown in figure 6. In spite of the higher amorphous contents of BA1 and BA2, BA3 had slightly higher compressive strength than BA1 and BA2. Higher strength for BA3 mortar specimens could be due to extended curing period than BA1 and BA2 and less water demand. However, the lime mortar compressive strength was

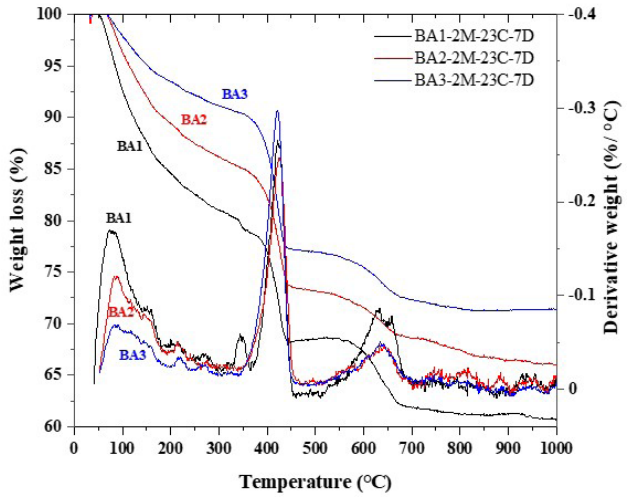


**Figure 5:** TGA plot for the binder from heat of hydration study (2M).

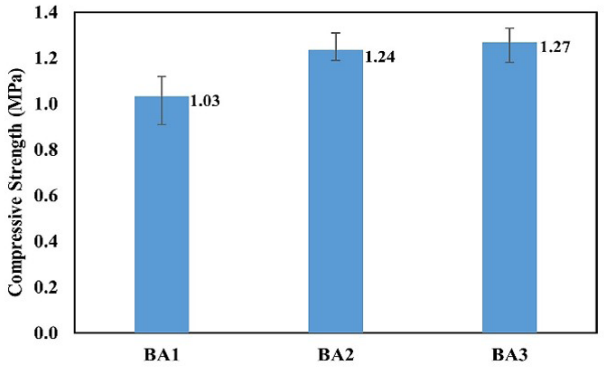


**Figure 6:** Lime mortar compressive strength from lime reactivity test (IS 1727).

around 1 MPa for all the ashes, which is much less than 4.5 MPa to pass the lime reactivity test as per IS 3812 [16].

## Conclusion

The agro-based biomass ashes collected were characterized for chemical and mineralogical composition, and reactivity assessment. The specific gravity of the ashes lies in the range of 2.0 - 2.2 and LOI values range between 3-14%, after passing through 300 m. The sum of oxide composition ($SiO_2$, $Al_2O_3$, and $Fe_2O_3$) for all the ashes fulfilled the chemical oxide requirement of Class F pozzolan as per ASTM C 618. However, the LOI values exceed the limits in the codal provisions [15, 16]. The mineralogical composition analysis showed BA1, BA2, and BA3 had 87%, 93%, and 77% amorphous content (includes the unburnt carbon) indicated by the amorphous hump between 20 - 30° (2θ). The particle size distribution is quite similar for all the three ashes. The reactivity of the ashes was assessed with heat of hydration study at ambient temperature and lime reactivity test as per IS 1727. The heat of hydration study revealed that BA2 has better reactivity than BA1, followed by BA3. The lime reactivity test showed a similar performance between BA1, BA2, and BA3. BA3 had a marginal increase in lime mortar strength that could be due to the extended curing period and less water demand. The reactivity assessment as per heat of hydration study showed that ashes with higher oxide content ($SiO_2$ + $Al_2O_3$ + $Fe_2O_3$) and amorphous content resulted in higher reactivity. BA3 exhibited the lowest heat of hydration despite the lower LOI value, which might be due to higher calcining temperatures that resulted in the formation of crystalline phases like cristobalite. Although BA1 and BA2 had higher LOI values than BA3, the amorphous content of the ashes resulted in enhanced reactivity. The limits for LOI values for SCMs to be used in the Portland cement system may not be considered for alternative cementitious binders. However, the performance of such binders including ashes with high LOI values (>10%) needs to be studied.

## Future work

The heat of hydration experiment needs to be performed at higher temperature (50 °C) for better degree of reaction and to compare the reactivity of biomass ash with other SCMs. In lime reactivity test, the lime-pozzolan mortar cubes should be cured at higher temperature before demolding to facil-

itate demolding for slow reacting SCMs. The dissolution of ash in alkaline medium will be further studied to understand the dissolution kinetics of biomass ash in low-molar alkaline medium. Further, binder will be prepared will high volume of biomass ash activated with Ca-Na based activators to study their performance.

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## Conflict of Interest

None.

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